

# PATENT SPECIFICATION

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## (54) PREPARATION OF 1,4-BUTANEDIOL

- (71) We, NISSAN KAGAKU KOGYO KABUSHIKI KAISHA, a corporation organized under the laws of Japan, of No. 7-1, 3-Chome, Kanda-Nishiki-cho, Chiyoda-ku, Japan, formerly of No. 2-2, 1-Chome, Nihonbashihon-cho, Chuo-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to a process for the preparation of 1,4-butanediol from  $\gamma$ -butyrolactone.
- 1,4-Butanediol is a known compound, and is useful as a solvent or plasticizer for epoxy resins, as a raw material in the manufacture of polyurethane fibres, and as an intermediate in the manufacture of tetrahydrofuran.
- According to the present invention, there is provided a process for the preparation of 1,4-butanediol, which comprises reducing  $\gamma$ -butyrolactone with hydrogen at a temperature of from 180 to 230°C. in the presence of a copper oxide-chromium oxide catalyst.
- The  $\gamma$ -butyrolactone used in the process of the invention can be easily and cheaply obtained by the reduction of maleic anhydride with hydrogen.
- It has been found that the reaction temperature greatly effects the yield of 1,4-butanediol in the above-described reaction, and that it is necessary to keep the reaction temperature in the range of from 180—230°C to selectively produce 1,4-butanediol economically in a high yield. If a copper oxide-chromium oxide catalyst is used for the reduction of  $\gamma$ -butyrolactone at temperatures higher than 150°C, but lower than 180°C, 1,4-butanediol is produced too slowly. For example, the rate of formation of 1,4-butanediol at 170°C is only about 40% of the rate at 200°C, and at 150°C it is less than one tenth of the former. Thus the use of such temperatures is not suitable for commercial production. On the other hand, at temperatures higher than 230°C, the activity of the catalyst quickly decreases and its ability to reduce the  $\gamma$ -butyrolactone is lost within a few hours. By analysing the residue of the catalyst used at such high temperatures, it has been found that some metallic copper is formed. Accordingly, at such high temperatures, the yield is low, and the catalyst cannot be reused without regeneration.
- It is known that a copper oxide-chromium oxide catalyst which has lost its activity can be regenerated by roasting in air, but it is troublesome and uneconomic to roast the catalyst after one or two cycles. Furthermore, the activity cannot be restored sufficiently by roasting in air.
- In the present invention, therefore, the reaction temperature used is from 180°C to 230°C. In this temperature range, not only can 1,4-butanediol be obtained in a high yield, but also reduction of the activity of the copper oxide-chromium oxide catalyst can almost be avoided, and the life of the catalyst can be remarkably prolonged.
- The copper oxide-chromium oxide catalyst is frequently used as a catalyst for manufacturing higher alcohols by the reduction with hydrogen of higher fatty acid esters and for other reductions. In these reduction processes, it is usual to use the catalyst at a comparatively high temperature i.e. higher than 230°C, but a rapid decrease of the activity of the catalyst at such a temperature is not observed.
- In the reduction with hydrogen of  $\gamma$ -butyrolactone, however, the activity abruptly decreases at temperatures higher than 230°C, as described above. This abrupt decrease of the activity is a peculiar phenomenon in the reduction of  $\gamma$ -butyrolactone, and was first observed by the inventors of the present invention.
- The copper oxide-chromium oxide catalyst used in the process of the present invention can be prepared by the process described by Adkins et al in the "Journal of the American Chemical Society" Vol. 54. 1092 (1931). Since that time, many modified processes for the preparation of copper oxide-chromium

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oxide catalysts have been described and a better result may be obtained by the use of a catalyst prepared by such a process.

5 The process of the present invention is preferably carried out at a hydrogen pressure of 50—300 kg/cm<sup>2</sup>, more preferably 100—250 kg/cm<sup>2</sup>. Under the conditions described above, the hydrogenation reaction takes place in the liquid phase, and it is preferable to use 10 the copper oxide-chromium oxide catalyst in an amount of more than 15% by weight, based upon the weight of  $\gamma$ -butyrolactone in the system. The reaction time is usually from 3 to 10 hours, although it varies depending on 15 the particular catalyst and the reaction condition used.

In the crude 1,4-butanediol produced by the process of the invention, a very small amount of high boiling-point materials are believed to be present, apart from the unreacted  $\gamma$ -butyrolactone. However, monocarboxylic acids such as propionic acid and butyric acid, and monalcohols such as propanol and butanol, have not been found. 20 Therefore, 1,4-butanediol of very high purity can be easily recovered from the crude product by distillation.

The invention will now be illustrated by the following Examples. Example 3 hereinafter is 30 not in accordance with the invention, and is included for comparison purposes only.

#### EXAMPLE 1

126 grams of ammonium bichromate were dissolved in 500 ml of water, and concentrated ammonia liquor was added to the solution until the colour of the solution changed from orange to yellow. This solution was cooled to room temperature, and a solution of 241.6 grams of copper nitrate trihydrate in 300 ml of water was added with agitation. 40 The reddish brown precipitate formed was filtered with suction, and dried at about 100°C for 24 hours. The product was pulverized and roasted at about 250°C to form a copper oxide-chromium oxide catalyst. 45

In a 300 ml autoclave, fitted with an electromagnetic stirrer, 60 grams of  $\gamma$ -butyrolactone and 12 grams of the above-described copper oxide-chromium oxide catalyst were introduced. 50

The autoclave was rapidly heated to 200°C, and, immediately, hydrogen was introduced at a pressure of 120 kg/cm<sup>2</sup> with stirring. The reaction was allowed to proceed 55 for 8 hours with the continuous introduction of hydrogen. After cooling, the contents of the autoclave were removed, and the catalyst was filtered off. The filter cake was washed with ethanol, and the previously obtained filtrate and the washing solution were mixed together. 1,4-Butanediol was found in the mixture. The yield of 1,4-butanediol was 54 grams, corresponding to 86% of the theoretical yield. 60

The filtered catalyst was washed and used a further four times in the manner described above. The yields of 1,4-butanediol obtained were from 85% to 89%. No appreciable decrease of the activity of the catalyst was observed. 65 70

#### EXAMPLE 2

In a 300 ml autoclave fitted with an electromagnetic stirrer, 60 grams of  $\gamma$ -butyrolactone and 12 grams of the same copper oxide-chromium oxide catalyst as used in Example 1 were introduced. The autoclave was rapidly heated to 180°C, and, immediately, hydrogen was introduced at a pressure of 250 kg/cm<sup>2</sup> with stirring. The reaction was allowed to proceed for 7 hours. After cooling, the contents of the autoclave were removed, and the catalyst was filtered off. The filter cake was washed with ethanol. The previously obtained filtrate and the washing solution were mixed together. 1,4-Butanediol was found in the mixture. The yield was 53 grams, which corresponds to 84% of the theoretical yield. 75 80 85

The filtered catalyst was washed and used a further four times in the manner described above. The yields of 1,4-butanediol were from 83% to 88%. No appreciable decrease of the activity of the catalyst was observed. 90

#### EXAMPLE 3

In a 300 ml autoclave fitted with an electromagnetic stirrer, 60 grams of  $\gamma$ -butyrolactone and 12 grams of the same copper oxide-chromium oxide catalyst as used in Example 1 were introduced. The autoclave was rapidly heated to 250°C, and, immediately, hydrogen was introduced at a pressure of 120 kg/cm<sup>2</sup>. The reaction was allowed to proceed for 8 hours. It was observed that about 2 hours after the start of the reaction, the absorption of hydrogen began to decrease abruptly, and 4 hours later, absorption of hydrogen had almost ceased. After cooling the autoclave, the contents were removed, and the catalyst was filtered off. The filter cake was further washed with ethanol. The previously obtained filtrate and the washing solution were mixed together. 1,4-Butanediol was found in the mixture. The yield of 1,4-butanediol was 23 grams, corresponding to 36% of the theoretical yield. 95 100 105 110

The filtered catalyst after washing was reddish in colour in contrast to the black colour of the catalyst before use, and the presence of metallic copper was found by x-ray analysis. 115

The recovered catalyst was used again in a manner similarly to that described above. No absorption of hydrogen could be detected, and it was clear that the activity of the catalyst had almost disappeared. 120

#### WHAT WE CLAIM IS:—

1. A process for the preparation of 1,4- 125

butanediol, which comprises reducing  $\gamma$ -butyrolactone with hydrogen at a temperature of from 180 to 230°C, in the presence of a copper oxide-chromium oxide catalyst.

5     2. A process according to claim 1, in which the reaction is carried out at a hydrogen pressure of from 50 to 300 kg/cm<sup>2</sup>.

10    3. A process according to claim 2, in which the reaction is carried out at a hydrogen pressure of from 100 to 250 kg/cm<sup>2</sup>.

4. A process for the preparation of 1,4-

butanediol, substantially as described in the foregoing Example 1 or Example 2.

5. 1,4-Butanediol whenever prepared by a process claimed in any one of the preceding 15 claims.

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